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(54) Title: METHODS AND APPARATUS FOR TREATING ELECTROLESS PLATING BATHS			
(57) Abstract			
<p>Apparatus and methods for removing formate ions from electroless metal plating baths employing formaldehyde as a reducing agent and typically comprising polyvalent anions as metal chelant and/or counterion. The apparatus and methods employ anion filtration to separate polyvalent anions from monovalent formate ions and ion exchange units to remove metal and metal chelant species from formate-containing streams. Preferred aspects of this invention provide apparatus and methods for removing formate from electroless copper plating baths.</p>			

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METHODS AND APPARATUS FOR TREATING
ELECTROLESS PLATING BATHS

Disclosed herein are methods and apparatus for treating electroless plating baths, e.g. removing by-product formate ions from electroless copper plating baths. Also disclosed are methods and apparatus for recycling materials from such baths and treating baths for disposal.

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BACKGROUND OF THE INVENTION

Plating baths for the electroless deposition of copper are common and typically comprise a copper salt, e.g. copper sulfate, a complexing agent such as EDTA and a formaldehyde reducing agent. As copper is depleted from such plating baths, formaldehyde is oxidized to formate ion and excess sulfate ions are generated. Copper ions and formaldehyde can be added to replenish a plating bath. Removal of formate and sulfate ions can be effected by withdrawing a purge stream. Besides the unwanted formate and sulfate ions, a purge stream also contains valuable species such as copper ions, formaldehyde and EDTA. Environmental awareness of the robustness of EDTA for the mobilization of toxic metals makes it less desirable to dispose of EDTA-containing solutions in waste streams.

Spent plating baths are traditionally treated by adding reducing agent such as sodium borohydride to precipitate elemental metal; residual soluble metal is precipitated with strong complexing agents, e.g. dithiocarbamate. Metal chelant complexes can be decomposed by oxidizing chelants, e.g. with peroxides, hypochlorates or other oxidizing acids.

Because of the difficulties in treating spent plating baths, disposal in landfills is often a method of choice for disposing of spent plating solutions or metal sludge precipitate from

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plating baths. For instance, metal recyclers often prefer to avoid spent electroless nickel solutions because of the high phosphorus content.

U.S. Patent 5,039,497 discloses methods of
5 removing copper from sulfate solutions using oximes.
Cognis, Inc. (Santa Rosa, California) has disclosed
that such an extraction process can be used to treat
copper and nickel electroless solutions to reduce the
metal content producing a solution suitable for
10 disposal, e.g. by sewerage. Such solvent extraction
methods have not been enthusiastically adopted for
treating plating baths comprising copper complexed
with EDTA, in part because common commercial
extractants are not especially effective in extracting
15 copper from complexes with EDTA.

Cardotte in US Patent 4,985,661 discloses
the use of hyperfiltration membranes to process copper
electroless plating solutions, e.g. to concentrate for
re-use salts of EDTA. Such membranes are more
20 permeable to formaldehyde and formate ions than EDTA
salts. It has been found that at a sufficiently high
level of copper, e.g. as is common in plating bath
purge streams, copper salts permeate such membranes
both as formate salts and EDTA salts. Such copper-
25 containing permeate streams are unsuitable for waste
disposal in many places. Moreover, such EDTA-
concentrated streams are typically unsuited for
recycle without further treatment, e.g. to remove
other anions, most commonly sulfate which is present
30 as the principal copper counterion.

SUMMARY OF THE INVENTION

This invention provides apparatus and
methods for removing formate ions from electroless
metal plating baths employing formaldehyde as a
35 reducing agent and typically comprising polyvalent
anions as metal chelant and/or counterion. The
apparatus and methods of this invention employ anion

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filtration to separate polyvalent anions from monovalent formate ions and ion exchange units to remove metal and metal chelant species from formate-containing streams.

5 Preferred aspects of this invention provide apparatus and methods for removing formate from electroless copper plating baths. These and other aspects and advantages of the subject matter of this invention will be apparent from the following detailed
10 description and illustrative examples.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

As used herein the term "chelant" means a compound which can form a water soluble metal complex, e.g. EDTA or tartrate are useful chelants for copper
15 in electroless copper plating baths. Compounds known as sequestrants are intended to be within the scope of the term chelant as it is used herein.

When formaldehyde is used as a reducing agent for electroless plating baths, metal deposition
20 is effected by simultaneous oxidation-reduction reactions. That is, metal is reduced as it is deposited while formaldehyde is oxidized to formate. For instance, cupric salt and formaldehyde are typically added to replenish electroless copper
25 plating baths with the result that such baths are progressively contaminated with oxidized reducing agent, e.g. formate ion, and excess copper counterion. Replenishment of metal species in such baths can be effected by electrolytic dissolution into a chelant solution. For instance, electroless copper plating
30 baths free of non-chelant counterion can be produced by electrolytically dissolving a copper anode in a chelant, e.g. tartrate, solution in the presence of a depolarizer, e.g. ammonia. Alternatively, a
35 concentrated copper salt can be provided by electrolytic dissolution on one side of a cationic permeable membrane, e.g., a Nafion membrane; a

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current passed through the cell or concentration effects will effect transfer of copper cations from the salt side of the membrane to a chelant solution on the other side of the membrane. While the generation 5 of excess metal counterion can be prevented, excess by-product formate ion must invariably be removed, typically by purging a working bath or treating the entirety of a spent bath.

Depending on the economic value of the metal 10 chelant and reducing agent, it is often desirable to separate and recycle the chelant and/or reducing agent from by-product species, e.g. oxidized reducing agent or excess counterion. Moreover, when formaldehyde-reduced electroless plating baths comprise polyvalent 15 chelant, the monovalent formate ion can be advantageously separated from polyvalent chelants by anion filtration using porous membranes having anionically functionalized surface. Such membranes are more selectively permeable to neutral and 20 monoanionic solutes and less permeable to polyvalent anionic solutes. Thus, monovalent counterions for metal and neutral formaldehyde species are removed with monovalent formate ions, but polyvalent counterions would be rejected along with polyvalent 25 chelants. An aspect of this invention provides methods for recycling metal as metal chelant species that are rejected by the anion filtration membrane. Because membranes are not absolute filters of 30 polyvalent anions, some metal chelant species will invariably permeate the membrane. In addition, some metal typically associated with formate ions will permeate the membrane. Thus metal associated with formate as a counterion and with polyvalent chelant will contaminate the formate-containing stream 35 rendering less suitable for disposal. This invention provides apparatus and methods for removing metal species from formate-containing streams.

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For example, a purge stream from a copper electroless plating bath will typically comprise cupric ions, formate ions, formaldehyde, polyanionic copper chelant species such as EDTA or tartrate and, unless otherwise provided by excess chelant or formate ions, a monovalent or polyvalent counterion for copper such a acetate or sulfate. Such solution can be conducted to a membrane filtration unit under sufficient pressure to effect permeation, resulting in a permeate stream and a residual stream. The concentration of formate ions and formaldehyde in the purge stream and residual stream will be essentially the same as in feed stream. The concentration of cupric ions will be lower in the purge stream and higher in the residual stream than in the feed stream. When a monovalent counterion such as acetate is present, its concentration tends to remain essentially unchanged like that of other monovalent permeable species. Polyvalent counterion species, when present, tend to concentrate with the metal-chelant species. Provided there is not an excess of free polyvalent counterion species, the residual stream containing metal-chelant species can generally be recycled to the electroless deposition bath. The permeate stream containing by-product formate ions can be conducted to an ion exchange unit to remove contaminant metal. When the chelant is one that strongly bonds to metal, e.g. with bonding on the order of the bonding to EDTA to copper, commonly available cation exchange resins are not suited for extracting the metal from the chelant complex. However, the metal-chelant complex is often sufficiently anionically charged as to be extracted as a unit using an anion exchange resin, a quarternary ammonium-functionalized resin such as e.g. Amberlite IRA-400 available from Rohm & Haas. When the chelant is one that weakly bonds to metal, e.g.

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with bonding on the order of the bonding to tartrate to copper, commonly available cation exchange resins, metal chelating resins functionalized with iminodiacetic acid (IDA) groups such as Amberlite IRC-5 718 resin available from Rohm & Haas, are generally suited for extracting the metal from the chelant complex.

Thus one aspect of this invention comprises conducting a formate-containing permeate stream to an ion exchange unit containing (i) a chelating ion exchange resin capable of removing metal ions from a solution in which said metal ions are complexed by a chelant having a binding energy on the order of the binding energy of copper tartrate or less or (ii) an anion exchange resin capable of removing metal chelant complexes from a solution in which said metal ions are complexed with a chelant having a binding energy on the order of the binding energy of copper EDTA, thereby providing a formate ion-containing stream which is essentially depleted of metal ions and metal chelant complexes. The effluent from such an ion exchange unit will also contain other monovalent anions and neutral compounds such as formaldehyde. Multi-staged membrane filtration can provide substantial enhancement of separation efficiency.

In another aspect of this invention it is sometimes desirable to separate and recycle metal as a first step, e.g. by delivering an electroless plating bath purge stream to a solvent extraction unit prior to anion filtration. Solvent extraction units typically comprise a series of mixing/settling vessels to provide intimate mixing and subsequent separation of an organic liquid and an aqueous liquid. Multi-staged extraction columns with countercurrent flow provide high efficiency liquid extraction. For example, an aqueous liquid comprising a purge stream

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from such an electroless copper plating bath comprising an aqueous solution of cupric ions, formate ions, formaldehyde and polyanionic cupric chelant species is intimately mixed with an organic liquid containing a cupric-extractant, e.g. in kerosene. During intimate mixing of aqueous and organic liquids, metal ions cross the phase boundary into the organic solution as a complex with the extractant. When mixing is stopped, the phases separate, e.g. in a continuous decanter apparatus. When a number of stages of such mixers and decanters are provided in a series, a high degree of efficiency can be attained, providing a metal ion-depleted aqueous stream and a metal-extractant organic stream. In summary, solvent extraction units typically comprise means for contacting a metal-containing feed stream with an organic solvent solution and means for separating an organic stream containing metal-extractant complex and an aqueous stream depleted in said metal species.

Effective solvent extraction requires the use of an extractant which exhibits a binding energy in a metal-extractant complex that is greater than the binding energy of the metal ions to the metal chelant species in the electroless plating bath. For instance, the bond strength of EDTA-copper complexes is sufficiently high as to resist copper extraction by common extractants, e.g. oximes. Preferred metal extractants for use in this invention are hydroxamic acids which are advantageously capable of extracting copper from EDTA complexes. Preferred hydroxamic acids with enhanced hydrolytic stability for cost effective long term use include N-alkyl alkanohydroxamic acids, e.g. N-methyl alkylhydroxamic acids, N-ethyl alkyl hydroxamic acids. Especially preferred are N-ethyl hydroxamic acids disclosed in U.S. patent application Serial No. 07/890,882.

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In this method of recycling metal, an organic stream containing metal-extractant complex is contacted with an acid stream to provide an aqueous stream having dissolved therein the metal salt of the stripping acid. When it is desired to recycle recovered metal directly into the plating bath, useful acids include any of the acids corresponding to the metal counterions or chelant used in the bath.

Because solvent extraction processes are seldom 100% effective in removing metal, the metal ion-diminished aqueous stream from the solvent extraction step may contain sufficient metal, e.g. as metal-chelant complex, to preclude its direct disposal, e.g. in municipal sewerage treatment facilities. Such residual metal-chelant complexes can often be removed by reducing the pH of the metal ion-diminished aqueous stream, e.g. to pH less than 2, to selectively form a precipitate of polyanionic metal chelant species which is readily removed by settling, filtration, centrifugation, etc. Removal of such precipitate provides a substantially cupric chelant-depleted stream. Trace amounts of metal, e.g. copper complexed with a moderate chelant such as tartrate, can be removed by conducting the solvent extracted stream to an ion exchange unit containing a chelating ion exchange resin.

Regardless of recycling method, e.g. anion filtration or solvent extraction, it is generally preferred to reduce the pH of the purge stream to increase its stability against autocatalytic deposition of metal.

The preferred method for treating sulfate-free plating bath to allow recycling of valuable materials while producing an environmentally acceptable, i.e. biodegradable, waste stream depends on the chelant. For instance, with baths containing

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moderate chelant, e.g. tartrate, the initial treatment of a purge stream can be either (i) anion filtration with recycle of the residual stream and the permeate stream being treated by chelant precipitation, if
5 necessary, followed by ion exchange or (ii) liquid extraction where the raffinate stream is treated by chelant precipitation and ion exchange. With baths containing strong chelants, e.g. EDTA, the initial treatment is preferably anion filtration which allows
10 recycle of valuable EDTA as a copper complex; the chelant in the permeate stream can be concentrated by reverse osmosis or destroyed, followed by ion exchange.

While the following examples illustrate the use of various materials in embodiments of plating solutions and methods of this invention, it should be clear from the variety of species illustrated that there is no intention of so limiting the scope of the invention. On the contrary, it is intended that the breadth of the invention illustrated by reference to the following examples will apply to other embodiments which would be obvious to practitioners in the plating arts.

EXAMPLE 1

25 This example illustrates the removal of tartrate from an electroless copper plating solution comprising 0.063 M cupric ion, 0.2 M tartrate, 0.18 M formaldehyde, 1.15×10^{-4} M cyanide at pH 12.4. The solution was mixed with a 12% solution of N-ethyl
30 decanohydroxamic acid in kerosene and allowed to settle, separating into two phases. Although phase separation was somewhat slow, separation was essentially complete with essentially no copper in the aqueous phase.

35 With a plating bath of similar composition but of pH of 8-10, phase separation was more rapid

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with essentially no residual copper in the aqueous phase.

When the procedure is repeated using EDTA, QUADROL, or NTA in place of tartrate, copper separation was significantly slower. Depending on the pH little or no copper extraction was effected. But with higher concentrations of hydroxamic acid, e.g. about 22%, enhanced copper extraction was demonstrated from solutions containing these stronger chelants.

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EXAMPLE 2

This example illustrates the solvent extraction of copper from a copper electroless plating bath where the copper was chelated with tartrate. A purge stream from the plating bath containing 3260 ppm Cu was fed to a two stage solvent extraction unit comprising two mixer-settler devices configured for one stage of extraction and one stage of stripping. That is extraction of copper from an aqueous stream into an organic extractant phase was conducted in the first mixer-settler and stripping of copper from the organic phase with an acid was conducted in the second mixer-settler. The feed flow rate of copper bath purge into the extraction stage was 20.0 ml/min. An extraction solution was prepared by dissolving 12 wt % N-ethyl decanohydroxamic acid in an organic solvent mixture of 95 vol % high flash point kerosene (Kermac 470 B) and 5 vol % isodecyl alcohol. The flow rate of the organic extraction solution back and forth between the extraction stage and stripping stage was also 20.0 ml/min. The stripping solution was 10 % sulfuric acid strip acid had a flow rate of 0.67 ml/min to the stripping stage. The mixer size was 640 ml for the extraction circuit and 180 ml for the strip circuit. The extraction settler was 640 ml and the strip settler was 450 ml.

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The solvent extraction unit was operated at the described flow rates; when steady state conditions were attained the raffinate, i.e. the aqueous effluent from the extraction mixer-settler, had a copper 5 concentration of 11 ppm. The copper sulfate effluent from the strip mixer-settler had a copper concentration of 99,300 ppm which was successfully used to prepare another electroless copper plating bath.

10

EXAMPLE 3

This example illustrates the recovery of tartrate from a copper electroless plating bath. A volume of raffinate from the extraction stage described in Example 1 was adjusted to pH 3.5 at room 15 temperature whereupon potassium hydrogen tartrate crystals started to form. Crystallization was complete after one hour where 75% of the tartrate had crystallized out of solution. Cooling increased the recovery further. Experience indicates that pH 3.0 is almost as effective as pH 3.5 but that pH 2.5 results 20 in a only 65% tartrate crystallization at room temperature. Experience with small volumes also indicates that about 50 minutes is required for optimum crystallization. Additional cooling, e.g. to 25 about 15 °C, enhances the amount of crystallization. The resulting "cream of tartar" crystals (potassium-hydrogen tartrate) quickly settle producing a clear supernatant which can be withdrawn easily without the need for filtration. The cream of tartar crystals readily redissolved in caustic solution producing a 30 clear tartrate solution which was used effectively in the formulation of new copper-tartrate plating bath.

After removal of the cream of tartar crystals, the supernatant liquid was withdrawn and

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passed through a chelating resin (Amberlite IRC-718). The copper concentration was reduced from 11 ppm to below the analytical detection limit of 0.1 ppm.

EXAMPLE 4

5 This example illustrates the recovery of copper-EDTA complex from rinse water used to remove electroless copper plating bath from plated parts. A volume of Cu-EDTA plating rinse solution (11.3 ppm Cu) was passed through an OSMONICS ST10 reverse osmosis
10 membrane at 500 psi. As the incremental volumes of the solution were passed through the membrane the retainate, permeate and filtered permeate were analyzed for copper concentration. The results shown in Table 1 show that reverse osmosis is effective in
15 concentrating copper(II)EDTA complex.

Table 1
COPPER CONCENTRATION

	RECOVERY %	RETAINATE ppm	FILTERED PERMEATE ppb	
			PERMEATE ppb	PERMEATE ppb
	0	11.3	-	-
	8	12.4	3	3
	50	23.5	7	8
25	75	46.1	28	13
	80	56.8	31	8
	85	76.4	46	10
	90	124.5	92	18

30 While specific embodiments have been described herein, it should be apparent to those skilled in the art that various modifications thereof can be made without departing from the true spirit and

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scope of the invention. Accordingly, it is intended that the following claims cover all such modifications within the full inventive concept.

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WHAT IS CLAIMED IS:

1. Apparatus for removing formate ions from aqueous solutions comprising dissolved metal associated polyvalent counterions and/or chelants,

5 comprising:

(a) a membrane filtration unit which is selectively permeable to monovalent anionic species,

10 (b) means for conducting said solution to said membrane filtration unit under sufficient pressure to provide a permeate stream and a residual stream wherein the concentration of formate ions is essentially the same in the purge, permeate and residual streams and the concentration of metal ions is lower in the permeate stream and higher in the

15 residual stream,

20 (c) an ion exchange unit containing (i) a chelating ion exchange resin capable of removing metal ions from a solution in which said metal ions are complexed by a chelant having a binding energy on the order of the binding energy of copper tartrate or (ii) an anion exchange resin capable of removing metal chelant complexes from a solution in which said metal ions are complexed with a chelant having a binding energy on the order of the binding energy of copper

25 EDTA,

(e) means for conducting said permeate stream to said ion exchange unit to provide a stream essentially depleted of metal ions and metal chelant complexes.

30 2. Apparatus according to claim 1 wherein, when said solution is an electroless copper plating solution, said apparatus further comprises means for adjusting the pH of said solution prior to conducting the solution to said membrane filtration unit.

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3. A method for removing formate ions from aqueous solutions comprising dissolved metal associated polyvalent counterions and/or chelants, comprising:

5 (a) conducting said solution to a membrane filtration unit which is selectively permeable to monovalent anionic species, wherein said solution is under sufficient pressure in contact with said membrane unit to provide a permeate stream and a
10 residual stream wherein the concentration of formate ions is essentially the same in the purge, permeate and residual streams and the concentration of metal ions is lower in the permeate stream and higher in the residual stream, and

15 (b) conducting said permeate stream to an ion exchange unit containing (i) a chelating ion exchange resin capable of removing metal ions from a solution in which said metal ions are complexed a chelant having a binding energy on the order of the binding energy of copper tartrate or (ii) an anion exchange resin capable of removing metal chelant complexes from a solution in which said metal ions are complexed with a chelant having a binding energy on the order of the binding energy of copper EDTA,
20 thereby providing a stream essentially depleted of metal ions and metal chelant complexes.

25 4. A method according to claim 3 wherein said aqueous solution is a copper electroless plating solution and said residual stream is recycled to said plating solution.

30 5. Apparatus for removing formate ions from an aqueous solution comprising metal associated with a polyvalent counterions or chelant, said apparatus comprising:

35 (a) a solvent extraction unit comprising an organic solvent solution of a metal extractant for removing metal as a metal-extractant complex, wherein

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the metal extractant exhibits a binding energy in a metal-extractant complex that is greater than the binding energy of said metal to the polyvalent chelant species, wherein said solvent extraction unit contains
5 means for contacting a metal-containing feed stream with said organic solvent solution and means for separating an organic stream containing metal-extractant complex and an aqueous stream depleted in said metal species;

10 (b) means for reducing the pH of the aqueous stream depleted in said metal species to selectively form a precipitate of the metal chelant species;

(c) means for separating precipitate of the metal chelant species to provide a stream
15 substantially diminished in metal chelant species;

(d) a membrane filtration unit which is selectively permeable to monovalent anionic species,

(e) means for conducting said stream substantially diminished in metal chelant species to
20 said membrane filtration unit under sufficient pressure to provide a permeate stream and a residual stream wherein the concentration of formate ions is essentially the same in the feed, permeate and residual streams and the concentration of polyvalent anions is lower in the permeate stream and higher in
25 the residual stream,

(f) an ion exchange unit containing (i) a chelating ion exchange resin capable of removing metal ions from a solution in which said metal ions are complexed a chelant having a binding energy on the order of the binding energy of copper tartrate or (ii) an anion exchange resin capable of removing metal chelant complexes from a solution in which said metal ions are complexed with a chelant having a binding

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energy on the order of the binding energy of copper EDTA,

5 (e) means for conducting said permeate stream to said ion exchange unit to provide a stream essentially depleted of metal ions and metal chelant complexes.

10 6. Apparatus according to claim 5 wherein, when said solution is an electroless copper plating solution, said apparatus further comprises means for adjusting the pH of said solution prior to conducting the solution to said solvent extraction unit.

15 7. A method for removing formate ions from an aqueous solution comprising metal associated with a polyvalent counterions or chelant, said apparatus comprising:

20 (a) delivering said solution to a solvent extraction unit comprising an organic solvent solution of a metal extractant for removing metal as a metal-extractant complex, wherein the metal extractant exhibits a binding energy in a metal-extractant complex that is greater than the binding energy of said metal to the polyvalent chelant species, wherein said solvent extraction unit contains means for contacting a metal-containing feed stream with said organic solvent solution and means for separating an organic stream containing metal-extractant complex and an aqueous stream depleted in said metal species, thereby providing an aqueous stream diminished in said metal species;

25 30 (b) reducing the pH of the aqueous stream diminished in said metal species to selectively form a precipitate of the metal chelant species;

35 (c) separating said precipitate of the metal chelant species to provide a stream substantially depleted in metal chelant species;

(d) conducting said stream substantially depleted in metal chelant species to a membrane

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filtration unit which is selectively permeable to monovalent anionic species as a feed stream under sufficient pressure to provide a permeate stream and a residual stream wherein the concentration of formate ions is essentially the same in the feed, permeate and residual streams and the concentration of polyvalent anions is lower in the permeate stream and higher in the residual stream,

(c) conducting said permeate stream to an ion exchange unit containing (i) a chelating ion exchange resin capable of removing metal ions from a solution in which said metal ions are complexed a chelant having a binding energy on the order of the binding energy of copper tartrate or (ii) an anion exchange resin capable of removing metal chelant complexes from a solution in which said metal ions are complexed with a chelant having a binding energy on the order of the binding energy of copper EDTA, thereby providing a stream containing formate ions and essentially depleted of metal ions and metal chelant complexes.

8. A method according to claim 7 wherein said aqueous solution is a copper electroless plating solution and said organic stream containing metal-extractant complex is stripped using an acid to provide a metal-bearing stream which is recycled to said plating solution.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/11020

A. CLASSIFICATION OF SUBJECT MATTER

C 02 F 9/00, B 01 D 61/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B 01 D 15/00, B 01 D 61/00, C 02 F 1/00, C 02 F 9/00,
C 23 C 18/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4 076 618 (ZEBLISKY) 28 February 1978 (28.02.78), claims 1,7,8,10,27,32. ----	1-8
A	US, A, 4 895 661 (CADOTTE) 23 January 1990 (23.01.90), claims 1-4. -----	1-3

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Date of the actual completion of the international search

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ANNEX

ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

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La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visé ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4076618	28-02-78	AT A 4784/77 AT B 353072 AU A1 26238/77 AU B2 511707 BR A 7704256 CA A1 1082376 CH A 630057 DE A1 2730322 DE B2 2730322 DE C3 2730322 DK A 3118/77 DK B 149617 DK C 149617 ES A1 460543 ES A5 460543 FR A1 2357287 FR B1 2357287 GB A 1533219 IL A0 52479 IL A1 52479 IT A 1079976 JP A2 53008333 JP B4 56054386 NL A 7707568 NL B 184048 NL C 184048 SE A 7707901 SE B 438871 SE C 438871 ZA A 7703059	15-03-79 25-10-79 04-01-79 04-09-80 06-06-78 22-07-80 28-05-82 02-02-78 02-07-81 29-04-82 10-01-78 11-08-86 12-01-87 01-10-78 11-10-78 03-02-78 09-03-79 22-11-78 31-10-77 31-07-80 16-05-85 25-01-78 25-12-81 11-01-78 01-11-88 03-04-89 10-01-78 13-05-85 22-08-85 26-04-78
US A 4895661	23-01-90	AU A1 10006/88 AU B2 610547 BR A 8800076 CN A 88100093 CN B 1011201 DE CO 3874554 DE T2 3874554 EP A2 274387 EP A3 274387 EP B1 274387 IN A 170561 JP A2 63190603 KR B1 9103115 US A 4834886	14-07-88 23-05-91 09-08-88 10-08-86 16-01-91 22-10-92 08-04-93 13-07-88 08-03-89 16-09-92 11-04-92 08-08-88 18-05-91 30-05-89